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Vibrational Spectra and Structure of Four-Membered Ring Molecules. IV. 2-Bromocyclobutanone and 2-Bromo-2,4,4-trideuterocyclobutanone

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The infrared and Raman spectra of 2-bromocyclobutanone and 2-bromo-2,4,4-trideuterocyclobutanone in the liquid state have been recorded. The far-infrared spectra of both compounds have also been recorded from 33–300 cm^{-1} in both the vapor and liquid states. The assignment of the 27 normal vibrations is given. The interesting ring-puckering vibration in 2-bromocyclobutanone has been observed at 153 cm^{-1} in the Raman spectrum and at 141.5 cm^{-1} in the infrared spectrum of the vapor. For the deuterium compound the corresponding absorption bands have been observed in the Raman and infrared spectra at 152 and 141 cm^{-1}, respectively. The data indicate that the potential function governing this vibration is only slightly anharmonic. No evidence has been found for the conformers previously reported for this molecule.

INTRODUCTION

The renewed interest in recent years in the nature of the potential function governing the ring-puckering vibration in four-membered ring molecules[1–10] has led to the study of 2-bromocyclobutanone and 2-bromo-2,4,4-trideuterocyclobutanone. In a far-infrared study of cyclobutanone and cyclobutanone-d_4[4,5] it was found that a pure quartic potential function would reproduce to within about one wavenumber all of the first seven transitions of the ring-puckering vibration with the exception of the ground-state transition. The cyclobutanone ring is considered to be essentially planar with a barrier to inversion of approximately 5 cm^{-1}. However, in a study of the Raman and infrared spectra of bromocyclobutane, the first upper-state transition was observed on the low-frequency side of the fundamental. It was therefore concluded that a broad potential function governs the ring-puckering vibration of bromocyclobutane.[6,10] The microwave investigation of bromocyclobutane[11] has shown that the ring is bent with a dihedral angle of approximately 29°.

The 2-bromocyclobutanone molecule has the carbonyl and bromine groups included on the same ring system. It was hoped that the effect of the simultaneous presence of these substituents on the nature of the potential function governing the ring-puckering vibration could be elucidated. Additional interest in this molecule arises from a recent publication by Conia and Gore.[12] They proposed the existence of two conformations for 2-bromocyclobutanone. In continuation of our study of the potential function governing the ring-puckering mode and the possible existence of conformers, we have investigated the Raman and infrared spectra of 2-bromocyclobutanone and its deuterium derivative, 2-bromo-2,4,4-trideuterocyclobutanone.

EXPERIMENTAL

The sample of 2-bromocyclobutanone was prepared by Perzanowski.[13] Liquid bromine was added dropwise for a period of 100 min to a solution of cyclobutanone in chloroform. The product was washed with $NaHCO_3$ and H_2O, and distilled. The collected fraction boiled at 70° and 10 mm Hg. The sample was purified with an Aerograph Model A90-P3 gas chromatograph with a 20-ft carbowax column under the following conditions: column temperature, 155°C; helium flow rate, 150 ml/min; injector, 200°C; detector, 220°C; collector, 240°C; bridge power, 150 mA. The collected fraction appeared to be better than 99% pure. The deuterated species was synthesized and purified by the procedure described above, except that cyclobutanone-d_4 was used as the starting material. The tetradeuterated ketone preparation has been described previously,[9] and the cyclobutanone-d_4 was shown by NMR to be greater than 99% isotopically pure before bromination.

The infrared spectra of the liquid samples were recorded from 240–4000 cm^{-1} with a Perkin-Elmer Model 521 spectrophotometer. Neat samples were examined between two CsBr disks. The infrared spectrum of liquid 2-bromocyclobutanone is shown in Fig. 1, and the observed frequencies are listed in Table I. The infrared spectrum of the deuterated molecule is shown in Fig. 2, and the frequencies are listed in Table II. The far-infrared spectra were measured on a Beckman

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* Taken in part from the thesis submitted by A. C. Morrissey to the Department of Chemistry in partial fulfillment for the degree of Ph.D.

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TABLE I. Infrared and Raman spectra of 2-bromocyclobutanone liquid.[a]

Infrared liquid (cm^{-1})	Relative intensity	Raman liquid (cm^{-1})	Relative intensity	Assignment
3640	w			$\nu_3+\nu_{21}=3651$
3566	m			$2\times\nu_6=3580$
3008(sh)	m	3010	vw	ν_1
		2980(sh)	w	ν_2
2965(brd)	s	2965(brd)	m	ν_3, ν_4
2934(sh)	m	2935	m	ν_5
2870	w			$2\times\nu_7=2884$
2765	vvw			$2\times\nu_8=2790$
2475	vvw			$\nu_6+\nu_{21}=2476$
2385	vvw			$2\times\nu_{11}=2390$
2300	vvw			$2\times\nu_{13}=2310$
2230	vvw			$\nu_9+\nu_{16}=2239$
2128(brd)	vvw			$2\times\nu_{14}=2139$
2050	vvw			$2\times\nu_{15}=2060$
1957	m			$\nu_{10}+\nu_{20}=1951$
1875(sh)	w			$\nu_{12}+\nu_{21}=1863$
1789	vvs	1790	m	ν_6
1752(sh)	m			$\nu_{10}+\nu_{22}=1768$
1725(sh)	m			$\nu_{12}+\nu_{22}=1733$
1620	vw			$\nu_{14}+\nu_{22}=1625$
1445	m	1445	w	ν_7
1393	s	1395	m	ν_8
1245(sh)	w	1247	w	ν_9
1211	s	1212	w	ν_{10}
1196(sh)	m	1195	w	ν_{11}
1177(sh)	m	1177	w	ν_{12}
1155	m	1155	vw	ν_{13}
1075	vw			$\nu_{22}+\nu_{23}=1071$
1063	v	1069	vw	ν_{14}
1029(sh)	w	1030	w	ν_{15}
990	m	991	w	ν_{16}
964	s	964	m	ν_{17}
892	m	894	m	ν_{18}
852	s	852	m	ν_{19}
737(sh)	w	739(brd)	w	ν_{20}
686	s	686	vs	ν_{21}
555	m	556	s	ν_{22}
513	s	515	s	ν_{23}
379	m	378	s	ν_{24}
		332	vvw	Impurity
270	m	266	vs	ν_{25}
152	m	153	vs	ν_{27}

[a] s, m, w, v, sh, brd, denote strong, medium, weak, very, shoulder, and broad, respectively.

IR-11 spectrophotometer[14] from 33 to 300 cm^{-1}. The recorded far-infrared spectra of the liquid samples, as 4% solutions (by volume) in benzene, were contained in polyethylene cells of 1 mm path. The measured frequencies are listed in Tables I and II, respectively. The far-infrared spectra of the vapor samples were recorded with a pressure of 10 torr in an 8.2-m-path cell equipped with polyethylene windows and heated to 70°C. Figure 3 shows tracings of the original far-infrared spectra of 2-bromocyclobutanone and 2-bromo-2, 4, 4-trideuterocyclobutanone, respectively. The observed frequencies in these spectra are listed in Table III.

Several attempts were made to record the vapor-phase spectrum in the mid-infrared region. However, a sufficient number of band envelopes was not resolved to merit reproduction of the recorded spectrum. The method used to purge and calibrate the infrared instruments has been previously described,[8] and the frequencies reported are expected to be accurate to ±2 cm^{-1} or better.

The Raman spectra were recorded on a Cary Model-81 Raman spectrophotometer which used a laser source. The spectra were recorded at the Applications Laboratory of Cary Instruments one year apart. During this time the instrument was continuously being modified and refined, and consequently, comparable conditions could not be attained and the spectra will not be reproduced. However, the observed Raman lines are listed in Tables I and II for the normal and deuterated species. The Raman spectra were not recorded on an

TABLE II. Infrared and Raman spectra of 2-bromo-2,4,4-trideuterocyclobutanone liquid.[a]

Infrared liquid (cm^{-1})	Relative intensity	Raman liquid (cm^{-1})	Relative intensity	Assignment
3635	w			$\nu_3+\nu_{19}=3618$
3564	w			$2\times\nu_6=3584$
3004(sh)	w	3010	w	ν_1
2963	m	2964	m	ν_3
2866	w	2868	w	$2\times\nu_7=2884$
2665	vvw			$\nu_5+\nu_{23}=2667$
2618	vvw			$\nu_{18}+\nu_{20}=2619$
2503	vvw			$\nu_6+\nu_{20}=2504$
2448	vvw			$\nu_2+\nu_{26}=2453$
2360	vvw			$\nu_4+\nu_{27}=2367$
2285	vvw			$\nu_6+\nu_{22}=2295$
2244(sh)	w	2243	w	ν_2
2213	m	2212	m	ν_4
2184	ms	2183	m	ν_5
2153(sh)	w	2152	w	$2\times\nu_8=2164$
2105	vw			$\nu_{13}+\nu_{17}=2105$
2038	vw			$\nu_7+\nu_{22}=2043$
2015	vw			$\nu_9+\nu_{16}=2012$
1880(sh)	vw			$2\times\nu_{11}=1890$
1785	vvs	1792	m	ν_6
1610	w			$\nu_{17}+\nu_{19}=1618$
1442	ms	1442	w	ν_7
1250(sh)	vw			$\nu_{15}+\nu_{26}=1245$
1228	m	1229	w	ν_9
1208(sh)	vw			$\nu_{11}+\nu_{25}=1207$
1140	ms	1140	w	ν_{13}
1084	s	1082	m	ν_8
1063(brd)	s	1063	w	ν_{14}
1054(sh)	w			$\nu_{20}+\nu_{24}=1056$
1033	s	1034	m	ν_{15}
963	m	965	w	ν_{17}
945	m	946(sh)	vw	ν_{11}
885	m	885	w	ν_{10}
826	m	827	s	ν_{18}
780	w	783	w	ν_{16}
711	m	712	m	ν_{20}
703(sh)	vw	704(sh)	vw	$\nu_{22}+\nu_{26}=712$
653	ms	653	w	ν_{19}
614	m	619	w	ν_{21}
498	m	503	s	ν_{22}
480(sh)	m	484	mw	ν_{23}
345	mw	344	m	ν_{24}
		329		Impurity
266	m	262	vs	ν_{25}
		210	w	ν_{26}
151	m	152	vs	ν_{27}

[a] s, m, w, v, sh, brd, denote strong, medium, weak, very, shoulder, and broad, respectively.

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[14] The far-infrared spectrophotometer was purchased with funds from National Science Foundation Grant GP-5827.

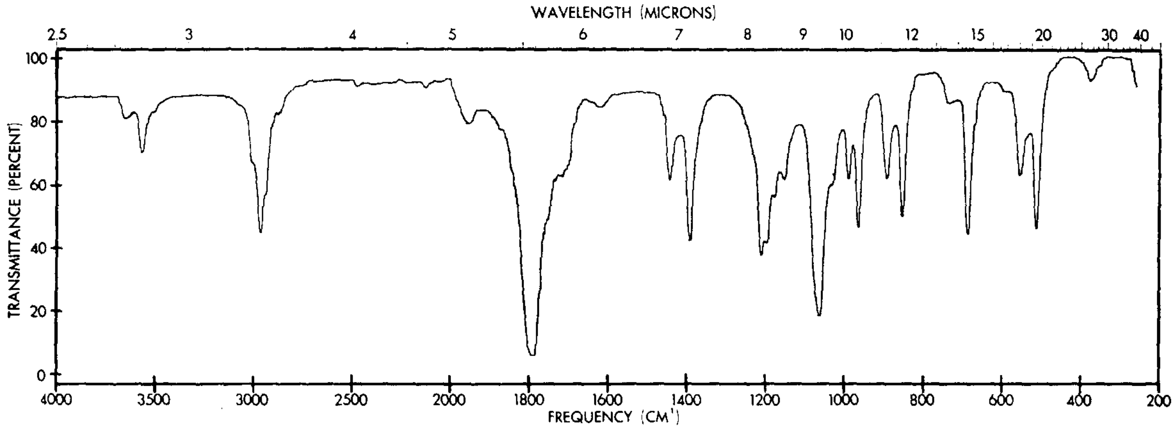


FIG. 1. Infrared spectrum of 2-bromocyclobutanone liquid phase. Recorded as liquid film.

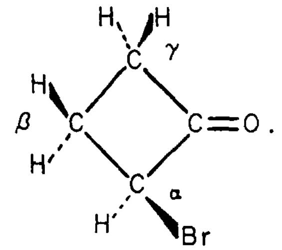
expanded scale, and the reported frequencies are not expected to be better than ±2 cm^{-1}.

DISCUSSION AND ASSIGNMENT OF FUNDAMENTALS

Since 2-bromocyclobutanone is devoid of symmetry, the molecule belongs to point group C_1. The 27 fundamental modes are Raman and infrared active. The lack of symmetry will permit all Raman lines to be polarized. Thus, depolarization values were of no assistance in assigning the fundamental modes of vibration and have not been included in the tables.

It was hoped that distinct band contours would be observed in the infrared spectrum of the vapor, but unfortunately most of the envelopes were not resolved. The low symmetry permits all normal modes to have simultaneous changes of the dipole moment along all three principal axes, and the resultant is a hybrid band. However, the isotopic shifts observed on deuterium substitution were invaluable in assigning the fundamental modes of 2-bromocyclobutanone and the deuterated compound. Information about the expected locations of analogous vibrations from the spectra of similar molecules, and the intensity of the Raman and infrared absorption bands were also used in making the vibrational assignments.

There is some question about the planarity of 2-bromocyclobutanone, but to alleviate confusion while discussing the various vibrational modes, it is assumed that the four ring carbons constitute a plane (molecular plane rather than a symmetry plane). The oxygen atom is included in the molecular plane with the remaining atoms out of the plane. The carbon atoms are denoted from the carbonyl group by the Greek letters α, β, and γ as shown below:



The discussion of the fundamental modes is catagorized

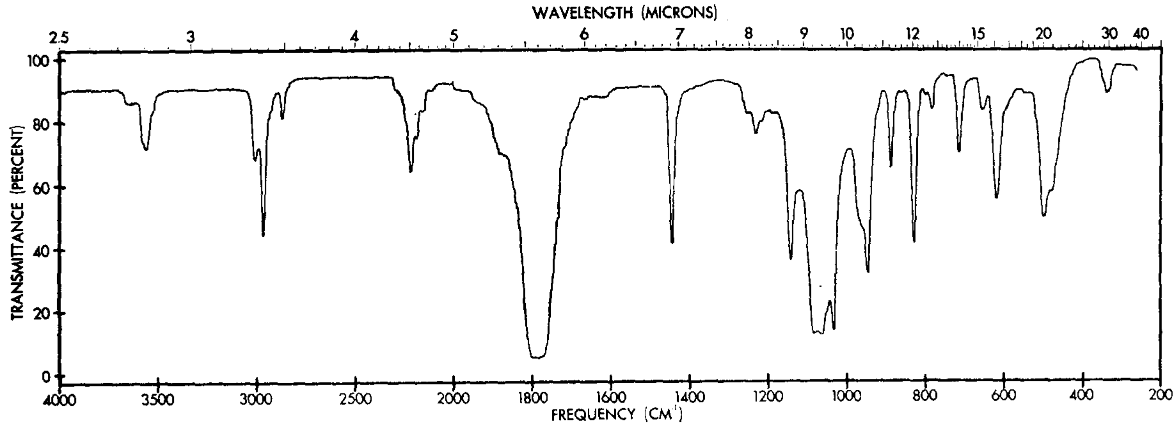


FIG. 2. Infrared spectrum of 2-bromo-2,4,4-trideuterocyclobutanone liquid phase. Recorded as liquid film.

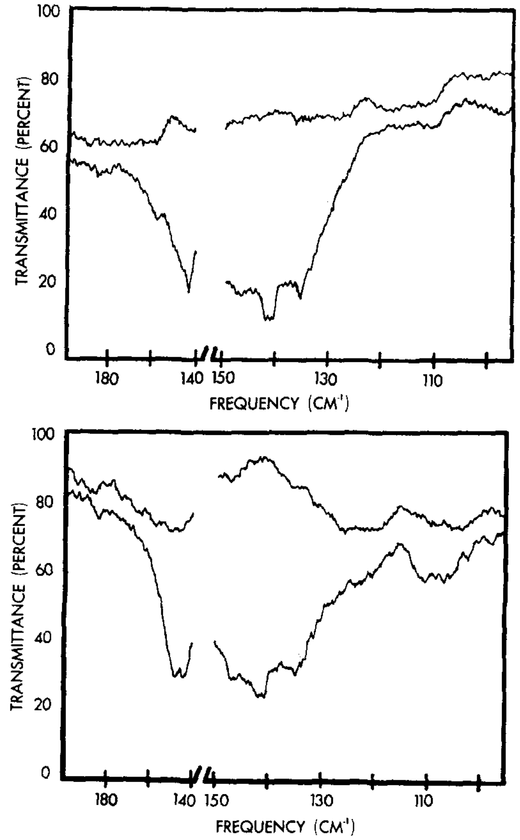


FIG. 3. Top: Far-infrared spectrum of 2-bromocyclobutanone vapor. Bottom: Far-infrared spectrum on 2-bromo-2, 4, 4-trideuterocyclobutanone. Recorded with 8.2 m path, pressure 10 torr at 70°C.

in the following manner: (1) carbon–hydrogen stretching vibrations, (2) carbon–hydrogen bending vibrations, (3) ring deformations, and (4) vibrations of the carbonyl and bromine groups.

Carbon–Hydrogen Stretching Vibrations

The deuterium substitution at the α and γ positions has made the assignment of the carbon–hydrogen stretching modes quite certain. The five C–H stretching motions are very nearly coincident in the Raman and infrared spectra. Three vibrations should shift on deuterium substitution and two should remain at relatively the same frequency. The β-CH_2 nonsymmetric and symmetric stretches are observed at 3010 and 2965 cm^{-1} in the Raman spectrum and do not shift with deuterium substitution. The γ-CH stretching vibration has been found as the highest frequency in analogous halocyclobutanes.[9,10] This vibration is expected to be weak and is assigned to the shoulder at 2980 cm^{-1} in the Raman spectrum of 2-bromocyclobutanone. The corresponding infrared band is masked by the strong absorption at 2965 cm^{-1}, but shifts to 2243 cm^{-1} with deuteration. The shift by a factor of 1.33 is approximately what one might expect for a C–H stretching vibration. The γ-CH_2 nonsymmetric stretching mode is always found at a higher frequency than the symmetric case, and it is believed to be on the low-frequency side of the strong absorption at 2965 cm^{-1}, which has been previously assigned to the β-CH_2 symmetric stretching mode. The assignment follows from that given for 2-chlorocyclobutanone,[15] in which the C–H stretching region is well resolved. With deuteration this vibration is observed at 2213 cm^{-1} in the infrared. The γ-CH_2 symmetric stretching mode is readily assigned to the Raman line of medium intensity at 2935 cm^{-1}, which shifts to 2183 cm^{-1} with deuteration. A shift by a factor of 1.34 is observed for both γ-CH_2 stretching modes.

Carbon–Hydrogen Bending Vibrations

There are 10 motions which can be adequately described as carbon–hydrogen bending vibrations. The β and γ hydrogens account for eight modes, and the remaining two are attributed to the lone α hydrogen. These vibrations are difficult to describe, unless one refers to the assumed molecular plane previously mentioned. The vibrations arising from the β-CH_2 hydrogens should not shift appreciably on deuteration, and consequently an assignment for these normal modes can readily be given. The Raman spectrum displays a line at 1445 cm^{-1} in the normal compound, which is assigned to the β-CH_2 deformation. The heavy molecule shows the corresponding Raman line at 1442 cm^{-1}. In the CH_2 wagging and twisting region, two bands at 1245 and 1155 cm^{-1} show only minor shifts to 1228 and 1140 cm^{-1}, respectively, with deuteration. In other studies of four-membered ring molecules, the methylene wagging motion has been found to be more

TABLE III. Far-infrared spectra of vapor 2-bromocyclobutanone and 2-bromo-2, 4, 4-trideuterocyclobutanone.[a]

Infrared gas (cm^{-1})	Band type	Intensity	Assignment
	2-Bromocyclobutanone		
272 *R*		m	
266 *Q*	A or C	s	ν_{25}
261 *P*		m	
147 *R*		m	
141.5 *Q*	A or C	s	$\nu_{27} 1 \leftarrow 0$
136 *P*		m	
135 *Q*	?	m	$\nu_{27} 2 \leftarrow 1$
	2-Bromocyclobutanone-d_3		
266 *R*		m	
260 *Q*	A or C	s	ν_{25}
254 *P*?		w	
147 *R*		ms	
141 *Q*	A or C	s	$\nu_{27} 1 \leftarrow 0$
135 *P*		m	
134 *Q*	?	m	$\nu_{27} 2 \leftarrow 1$

[a] Abbreviations used: s, strong; m, medium; w, weak; *P*, *Q*, *R*, refer to the rotational branches of a single band and A, B, C refer to the band type.

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[15] J. R. Durig and W. H. Green, "Vibrational Spectra and Structure of 2-Chlorocyclobutanone" (unpublished).

Table IV. Summary of fundamental frequencies of 2-bromocyclobutanone and 2-bromo-2,4,4-trideuterocyclobutanone.

Fundamental	Approximate description	2-Bromocyclobutanone (cm^{-1})[a]	2-Bromocyclobutanone-d_3 (cm^{-1})[a]
1	β-CH_2 nonsymmetric stretching	3010*	3010*
2	α-CH stretching	2980*	2244
3	β-CH_2 symmetric stretching	2965	2963
4	γ-CH_2 nonsymmetric stretching	2965	2213
5	γ-CH_2 symmetric stretching	2934	2184
6	C–O stretching	1789	1785
7	β-CH_2 deformation	1445	1442
8	γ-CH_2 deformation	1393	1084
9	β-CH_2 twisting	1245	1228
10	α-CH bending ($\perp$)	1212	885
11	γ-CH_2 wagging	1196	945
12	γ-CH_2 twisting	1177	945
13	β-CH_2 wagging	1155	1140
14	Ring deformation	1063	1063
15	Ring deformation	1029	1033
16	α-CH bending ($\parallel$)	990	780
17	Ring deformation	964	963
18	Ring deformation	892	826
19	γ-CH_2 rocking	852	653
20	β-CH_2 rocking	737	711
21	Ring deformation	686	614
22	C–Br stretching	555	498
23	C–O bending (in plane)	513	480
24	C–O bending (out of plane)	379	345
25	C–Br bending ($\perp$)	270	266
26	C–Br bending ($\parallel$)	(225)	210*
27	Ring puckering	152	151

[a] Numbers in parentheses have not been observed, but are estimated. All other values are infrared frequencies of liquid. Asterisk denotes Raman frequencies.

intense in the infrared spectrum and occurs at a higher frequency than the methylene twisting mode. Since the infrared spectra of the two molecules show the lower band to be more intense, we prefer to assign it to the β-CH_2 wagging mode and the band of higher frequency to the β-CH_2 twisting vibration. The fourth β-CH_2 bending mode can be described as a CH_2 rocking motion. The Raman spectra show lines at 739 and 712 cm^{-1} in the light and heavy molecules, respectively, and they are assigned to the β-CH_2 rocking vibration.

The assignment of the γ-CH_2 bending modes is based upon the observed shifts of these normal vibrations with deuteration. The deformation is assigned to the 1393-cm^{-1} infrared band, which shifts to 1084 cm^{-1} with deuterium substitution. The shift by a factor of 1.28 seems plausible for a CH_2 bending mode. The infrared bands at 1196 and 1177 cm^{-1} are believed to be the γ-CH_2 wagging and twisting modes, respectively. Although the intensity of these two bands is nearly the same, the assignment of the wagging motion to the band of higher frequency follows from the intensity of the corresponding strong band observed in the 2-chlorocyclobutanone spectrum.[15] It has been found that the frequencies for the normal modes for 2-chlorocyclobutanone correspond very well with those for 2-bromocyclobutanone, and the assignments for this molecule support the assignments for the bromo compound. The γ-CH_2 twisting is not uniquely observed for the deuterium compound, but a tentative assignment of 945 cm^{-1} which is accidentally degenerate with the CH_2 wagging mode is proposed. The γ-CH_2 rocking mode is assigned to the Raman line of medium intensity at 852 cm^{-1}, which shifts by 1.30 to the 653 cm^{-1} with deuteration. The corresponding infrared bands are at the same frequencies.

The α-CH bending modes have been observed at higher frequency for bromocyclobutane[10] and chlorocyclobutane[9] than one might expect. Similarly, the γ-CH bending (perpendicular-to-plane) mode for bromocyclobutanone is observed in the Raman spectrum at the relatively high frequency of 1212 cm^{-1}. The shift of 1.34 to the line at 885 cm^{-1} is large, but not unexpected for this vibration. The infrared band observed at 990 cm^{-1} in the light compound shifts to 780 cm^{-1} with deuteration. This absorption is attributed to the α-CH bending (parallel-to-plane) mode.

Ring Deformation

The six motions of the skeletal ring system can be approximately described as ring deformations. Five of these modes involve motions parallel to the assumed molecular plane, and these deformations are usually characterized by intense Raman lines. The intensity of the corresponding infrared absorption bands has been found to be dependent on the system and specific deformations.[16] The frequency and intensity of the strong infrared band at 1063 cm^{-1} suggest that it does not arise from a carbon–hydrogen bending vibration, but from a ring deformation which involves a large dipole change. The two medium-intense Raman lines at 1030 and 964 cm^{-1} are similarly assigned to ring deformations. These three ring deformations show negligible shifts in the deuterated molecule. The two intense Raman lines at 892 and 686 cm^{-1} are attributed to the two remaining planar ring modes. The corresponding Raman lines in the deuterated compound are found at 827 and 619 cm^{-1}, respectively. The shift is larger than one might expect for the ring deformations, and it suggests that these two modes are coupled with the bending vibrations of the methylene groups. The mixing of these two ring modes has been reported previously in the deuterated analogs of the halocyclobutanes.[9,10]

Perhaps the most interesting vibration of 2-bromocyclobutanone is the out-of-plane ring deformation normally referred to as the ring-puckering vibration. It is expected to be the band of lowest frequency and is assigned to the strong Raman line at 153 cm^{-1}. The corresponding band in the infrared spectrum of the vapor is expected to be at a slightly lower frequency than the absorption band of the liquid, and it is centered at 141.5 cm^{-1}. The band contour resembles a Type A envelope with P and R branches at 147 and 136 cm^{-1}, respectively. The only apparent "hot band" falls at 135 cm^{-1}, and is overlapped by the R branch (see Fig. 3). The deuterated compound displays the corresponding Raman line at 152 cm^{-1} while the far-infrared spectrum of the vapor shows the apparent Type A band at 141 cm^{-1}, with the R and P branches at 147 and 134 cm^{-1}, respectively. The only "hot band" observed is the sharp peak at 134 cm^{-1}, which is again overlapped by the P branch. The ring-puckering vibration shows negligible shift with deuterium substitution, which is somewhat surprising, since for other four-membered ring molecules, the corresponding vibration showed a marked shift with isotopic substitution. One explanation for this deviation would be to consider the ring-puckering vibration in 2-bromocyclobutanone as a motion of the β-CH_2 group perpendicular to the molecular plane with the other part of the molecule remaining essentially rigid. Such a vibration should not be greatly effected by deuterium substitution at the α and γ positions.

The spectra of both molecules display the only observed upper-state transition on the low frequency side of the fundamental mode. The position of the "hot band" indicates that the potential function governing the ring-puckering vibration is similar to that found for 3-methyleneoxetane,[8] but not nearly as anharmonic. Although the upper-state transitions of the ring-puckering vibration in 2-bromocyclobutanone and its deuterium analog are not definite enough for qualitative calculations, there is little question that the potential function is broader than the normal harmonic well. The implications of this potential function on the molecular structure are discussed further in a later section.

Carbonyl and Bromine Vibrations

The C=O stretching vibration, which is unquestionably assigned to the strong band in the infrared spectrum at 1789 cm^{-1}, displays a negligible shift with deuterium substitution. The two carbonyl-bending modes are assigned to the strong infrared bands at 513 and 379 cm^{-1}. The observed shift on deuterium substitution closely approximates what was reported for the cyclobutanone-d_4 molecule.[17] The 513-cm^{-1} band shifts to 480 cm^{-1}, and the one at 379 cm^{-1} shifts to 345 cm^{-1}. The parallel bending mode is attributed to the band of higher frequency, while the absorption band of lower frequency arises from the perpendicular motion.[17]

The carbon–bromine stretching vibration should show an intense Raman line, and it is readily assigned to the strong Raman line at 556 cm^{-1}. The shift to 503 cm^{-1} for the deuterated molecule suggests that the C–Br stretching vibration is strongly coupled with other low-frequency vibrations. The perpendicular and parallel bending motions of the halogen showed very strong and weak Raman lines, respectively, in the halocyclobutanes.[9,10] For 2-bromocyclobutanone the very strong Raman line at 266 cm^{-1} is assigned to the perpendicular C–Br bending motion. A shift of 4 cm^{-1} is observed with deuteration. The weak Raman line at 210 cm^{-1} in the heavy molecule is attributed to the parallel bromide bending mode. In the normal compound this Raman line has not been directly observed, but is estimated to fall near 225 cm^{-1} on the basis of the corresponding frequency shift observed for the bromocyclobutane molecule. The summary of the vibrational assignments of 2-bromocyclobutanone and 2-bromo-2,4,4-trideuterocyclobutanone with approximate descriptions of the normal modes are given in Table IV.

Combinations and Overtones

The absence of symmetry elements in this molecule permits all combinations and overtones to be active in both the Raman and infrared spectra. The large number of weak combinations and overtone bands (see Figs. 1

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and 2) makes unique assignments not feasible. However, reasonable assignments are given in Tables I and II for all observed frequencies.

SUMMARY AND CONCLUSIONS

As part of an extensive study of cyclobutanone chemistry, Conia and Gore[12] have proposed that 2-bromocyclobutanone exists in two conformations. The presence of conformers should be observed in the vibrational spectra as sidebands or as splitting of some of the fundamental modes. In our Raman and infrared investigation of 2-bromocyclobutanone and the deuterated counterpart, the appearance of sidebands or the splitting of fundamental absorption bands for even the most intense fundamentals has not been observed. The existence of axial and equitorial conformers in α-halocyclonones[18–20] has been deduced from the shift of the carbonyl stretching frequency in various solvents, and this technique was applied to 2-bromocyclobutanone by Conia and Gofe.[12] They state that the observed data indicate that the axial conformer is favored in nonpolar solvents and that the equitorial conformer is favored in polar solvents. Close examination of the data shows a trend that could be attributed not to the existence of conformers, but solely to the expected solvent effects. The dipole-moment data used by Conia and Gore to support the existence of conformers is thought to be within experimental limitations of such measurements. The precision of dipole-moment measurements in solution is altered by solvent effects, which introduce an absolute error up to 10% or more.[21]

The coupling constants observed in the NMR spectrum of 2-bromocyclobutanone were also used by Conia and Gore[12] to support the existence of conformers. They[12] also state that since the coupling constant $J_{\mathrm{HH}'}=J_{\mathrm{HH}''}=8.2$ cps for cyclobutanone, a $J\neq 8.2$ indicates that the ring is not planar. They report the coupling constants for 2-bromocyclobutanone are $J_{\mathrm{HH}'}=8.8$ cps (*cis*) and $J_{\mathrm{HH}''}=7.4$ cps (*trans*). From NMR data recorded in this laboratory, these coupling constants could not be substantiated. Roberts and Lambert[22] have recently commented that the similarity in coupling constants (6.4–9.7 cps) found by Conia *et al.*,[23] is very different from the wide range of hydrogen–fluorine couplings for cyclobutanes which are known to be puckered. Without temperature studies, Roberts and Lambert[22] indicate that it is impossible to distinguish between statistical and dynamic planarity by coupling-constant considerations alone, and they suggest that the deviation from planarity in the cyclobutanones is expected to be small.

As mentioned previously, the equilibrium configurations of cyclobutanone[4,5] and bromocyclobutane[11] have been established. The presence of the carbonyl group tends to increase ring strain and force planarity, while the bromide substituent tends to pucker the ring. The frequency of the C=O stretching mode is directly related to ring strain in cycloketones, where an increase in ring strain shows an increase in the C=O stretching frequency. Since bromine tends to pucker the ring, it seems reasonable to assume that the frequency of the C=O stretching mode should decrease with bromination. However, it is noted that the C=O stretching frequency in 2-bromocyclobutanone is 10 cm^{-1} higher than in cyclobutanone.[17] In cycloheptanone, where the ring strain is negligible, the C=O stretching frequency is 1705 cm^{-1} [24] and increases 3 cm^{-1} in α-bromocycloheptanone.[25] Thus, the increase in the C=O stretching frequency for 2-bromocyclobutanone can be attributed to the inductive effect bromine has on the carbonyl stretching frequency when it is an adjacent position, and there is no indication of relief of the ring strain by the bromine atom. The C–Br stretching frequency in 2-bromocyclobutanone also is higher by 62 cm^{-1} than that observed in bromocyclobutane.[10] From this fact alone it can be concluded that the tendency of the bromine atom to pucker the ring is small compared with the force exerted by the carbonyl group, which tends to force planarity.

The $1\leftarrow 0$ and $2\leftarrow 1$ transitions in cyclobutanone[4,5] were observed at 35 and 57 cm^{-1}, respectively, in the far-infrared spectrum of the vapor. In bromocyclobutane[10] the $1\leftarrow 0$ transition was observed at 143 cm^{-1}. The first "hot band" has been observed on the low-frequency side of the fundamental, and the generalized absorption "tailed-off" to lower frequency. The analogous vibration for 2-bromocyclobutanone showed an apparent Type A band in the far-infrared spectrum of the vapor centered at 141.5 cm^{-1}. The only observed "hot band" is at 135 cm^{-1}. It can be seen from the band shape and position of the upper-state transition that neither the asymmetric potential function[6] used to explain the tailing off of the ring-puckering vibration in bromocyclobutane[10], nor the large quartic term used to explain the potential function of cyclobutanone[4,5] is applicable to 2-bromocyclobutanone. Thus, one predicts that the potential function of the ring-puckering vibration is only slightly more anharmonic than those governing most normal modes of vibration, since the shape of the band, which arises from the ring-puckering

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vibration in 2-bromocyclobutanone, does not resemble that observed in bromocyclobutane.[10] Also, the previously stated arguments cast doubt on the interpretation of the data used to support the existence of conformers. Thus, it is concluded on the basis of our experimental data that the 2-bromocyclobutanone molecule is planar or very nearly so.

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New Absorption Spectra of Atomic and Molecular Oxygen in the Vacuum Ultraviolet. II. Rydberg Series from O I(${}^1D_2$) and O I(${}^1S_0$) Metastable States

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We have extended our previous work [J. Chem. Phys. **46,** 2213 (1967)] on absorption series from the O I ${}^3P_{2,1,0}$ ground state by measuring and classifying eight series having metastable O I ${}^1D_2$ or ${}^1S_0$ as the lower state. For O I ${}^1D_2$ as the lower state, series have been classified with the following upper states:

$({}^2D^0)ns'$: ${}^1D^0{}_2$, and ${}^3D^0{}_2$,
$({}^2D^0)nd'$: ${}^1F^0{}_3$, ${}^1D^0{}_2$, and ${}^1P^0{}_1$,
$({}^2P^0)ns''$: ${}^1P^0{}_1$,
$({}^2P^0)nd''$: ${}^1D^0{}_2$.

The one series with O I ${}^1S_0$ as the lower state has the upper state $({}^2P^0)nd''$ ${}^1P^0{}_1$. The classifications are tentative in some cases. The spectra were observed primarily in absorption through a microwave dischage of a dilute O_2 mixture with helium in a flow system using the Hopfield helium continuum (600–1000 Å) as background. New atomic energy levels for a number of O I singlet terms are given. The metastable ${}^1D_2$ and ${}^1S_0$ atoms disappear rapidly in the downstream region, and it is suggested that they react to form the metastable O_2 molecules ($a\ {}^1\Delta_g$ and/or $b\ {}^1\Sigma_g{}^+$) known to be present in the discharge products.

INTRODUCTION

In our previous paper[1] (Part I), we reported nine absorption series of ground-state atomic oxygen $2p^4\ {}^3P_{2,1,0}$ observed in the vacuum ultraviolet. Most of these lines and associated energy levels had not been reported in the extensive earlier work,[2–6] which was almost exclusively done in emission.

In this paper, we report measurement and classification of eight series with the metastable oxygen atoms $2p^4\ {}^1D_2$ and $2p^4\ {}^1S_0$ as the lower states. These series were observed either in the absorption or the emission spectrum of a microwave discharge in a very dilute oxygen mixture with helium, as we noted briefly in our earlier paper.[1] Most of these transitions and energy levels have not previously been reported. Many of the upper levels are autoionized, which makes them very difficult to observe in emission.

EXPERIMENTAL

The apparatus and technique are briefly described, since they are identical to those in the initial paper of this series.[1] The flow absorption system is shown in Fig. 1 of that paper. It is a 50-cm-long windowless absorption cell placed between the helium-continuum light source and the spectrograph entrance slit. A He–0.25% O_2 mixture entered the cell through a side-arm near the light source and was pumped through the cell with a 20-liter/sec mechanical pump. Atomic oxygen was formed by a microwave discharge positioned in the middle of the absorption cell. With this arrangement, discharge absorption spectra were obtained, while the downstream absorption spectra measured previously were obtained with the discharge on the entrance side-arm. A Raytheon Model PGM-100 microwave power supply (800 W maximum, 2450 Mc/sec)

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